PB82-242389

# PSD Monitoring

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

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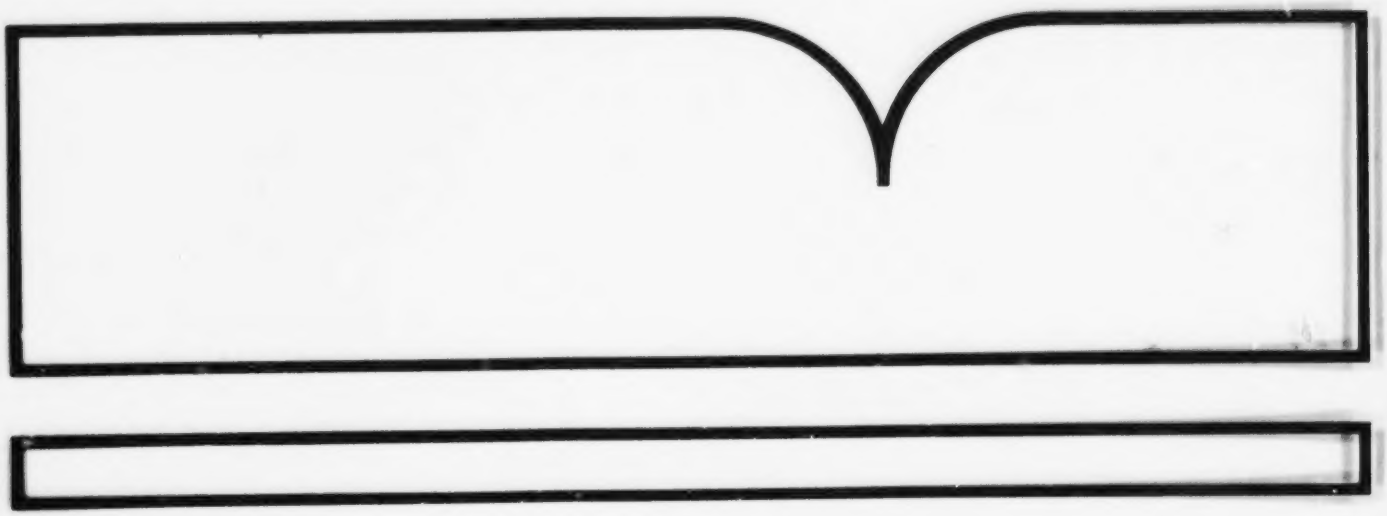

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This is a memo from Mr. Kenneth A. Rehme to Mr. Warren Peters, CPDD/OAQPS (md-15) on the subject of PSD Monitoring.

**16. ABSTRACT**

This is a memo containing information on PSD Monitoring. It includes tables showing PSD monitoring methods and averaging times for the regulated criteria and non-criteria pollutants. The Rationale for the PSD Monitoring De Minimis Concentrations is also given. (Bibliography).

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, NC 27711

DATE: May 20, 1980

SUBJECT: PSD Monitoring

FROM: Mr. Kenneth A. Rehme, Methods Standardization Branch, QAD/EMSL, (MD-77) KAR

TO: Mr. Warren Peters, CPDD/OAQPS (MD-15)

The following information pertinent to PSD monitoring regulations is provided in the attached tables and report as per your telephone requests of last week:

(1) Tables showing PSD monitoring methods and averaging times for the regulated criteria and non-criteria pollutants.

(2) Rationale for the PSD Monitoring De Minimis Concentrations.

If you have any questions regarding the tables or the rationale, contact me or Larry Purdue at your convenience.

Attachments

cc: T.A. Clark
T.R. Hauser
L.J. Purdue

TABLE I. CRITERIA POLLUTANTS

| Pollutant | Monitoring Method | Monitoring Method Averaging Time |
|---|---|---|
| CO | Designated reference or equivalent method[a] | Continuous |
| $NO_2$ | Designated reference or equivalent method[a] | Continuous |
| $SO_2$ | Designated equivalent method[a] | Continuous |
| $O_3$ | Designated reference or equivalent method[a] | Continuous |
| TSP | Reference method[b] | 24-hour |
| Pb | Reference method[c] or designated equivalent method[a] | 24-hour |

(a) See attached list of designated reference and equivalent methods.

(b) 40 CFR Part 50, Appendix B.

(c) 40 CFR Part 50, Appendix G.

TABLE II. NON-CRITERIA POLLUTANTS

| Pollutant | | Monitoring Method | Monitoring Method Averaging Time |
|---|---|---|---|
| Hg | * | Collection by charcoal adsorption; analysis by UV absorption[a] | 24-hour |
| Be | * | Collection by high-volume sampler; analysis by inductively coupled plasma optical emission spectrometry[b] | 24-hour |
| | * | Collection by high-volume sampler; analysis by UV fluorescence with morin[c] | 24-hour |
| | | Collection by high-volume sampler; analysis by flameless atomic absorption[d] | 24-hour |
| Asbestos | | No acceptable method | - |
| $H_2SO_4$ | | No acceptable method | - |
| Vinyl Chloride | * | Collection by charcoal adsorption; analysis by gas chromatography with flame ionization detector[e] | 24-hour |
| | | Collection in plastic bag; analysis by gas chromatography with flame ionization detector[f] | Grab sample |
| | | Collection in plastic bag; analysis by gas-liquid chromatography with mass spectrometry[g] | Grab sample |
| F | * | Collection and separation of gaseous and particulate F with $NaHCO_3$ coated glass tube and particulate filter; analysis by various techniques[h] | 24-hour |
| | * | Collection and separation of gaseous and particulate F with double paper tape sampler; analysis by various techniques[i] | 1-24 hours |
| | | Collection on $Na_2CO_3$ impregnated filters; analysis by specific ion electrode[j] | 1-24 hours |
| $H_2S$ | | Collection on $AgNO_3$ impregnated filters; analysis by fluorometry[k] | 30 min - 4 hours |
| | * | Collection by absorption in $Cd(OH)_2$; analysis by spectrophotometry[l] | 2-hour |
| | | Collection on gold coated glass beads; analysis by flame photometry[m] | 15 min - 1 hour |

| | | |
|---|---|---|
| TRS,RS | Analysis of total TRS by flame photometry as $SO_2$ (after oxidation); $SO_2$ removal by $NaHCO_3$ filter[n] | Semicontinuous |
| | Analysis of individual TRS species by gas chromatography/flame photometry after cold trap preconcentration[h] | Analysis every 30-min |
| | Analysis of individual TRS species by gas chromatography/flame photometry without preconcentration[o] | Analysis every 10-min |
| | Collection on gold coated glass beads; analysis by flame photometry[m] | 15 min - 1 hour |


(a) F. Scaringelli, J. C. Puzak, B. I. Bennett, and R. L. Denny. "Determination of Total Mercury in Air by Charcoal Adsorption and Ultraviolet Spectrophotometry." Anal. Chem., 46:278 (1974).

(b) D. R. Scott, W. A. Loseke, L. E. Holboke, and R. J. Thompson. "Analysis of Atmospheric Particulates for Trace Elements by Optical Emission Spectrometry." Applied Spectroscopy, *30:392* (1976).

(c) Intersociety Method No. 303, "Tentative Method of Analysis for Beryllium Content of Atmospheric Particulate Matter." Methods of Air Sampling and Analysis, Second Ed., American Public Health Association, 1977.

(d) A. Zdrojewski, L. DuBois, and N. Quickert. "Reference Method for the Determination of Beryllium in Airborne Particulate." The Science of the Total Environment, 6:165 (1976).

(e) EPA Tentative Method for the Determination of Vinyl Chloride in the Atmosphere (24-Hour Integrated Sampling). October 1974.

(f) E. Burghardt, R. Jeltes, H. J. van der Wiel, and E. J. Oranje. "A Direct and Sensitive Gas Chromatographic Method for Selective Measurement of Vinyl Chloride in Ambient Air." Atmospheric Environment, 13:1057 (1979).

(g) J. D. Rosen, et al. "Analysis of Vinyl Chloride by Mass Fragmentography." J. of the AOAC, 58:700 (1975).

(h) Intersociety Method No. 206, "Tentative Method of Analysis for Gaseous and Particulate Fluorides in the Atmosphere (Separation and Collection with Sodium Bicarbonate Coated Glass Tube and Particulate Filter)."

(i) Intersociety Method No. 207, "Tentative Method of Analysis for Gaseous and Particulate Fluorides in the Atmosphere (Separation and Collection with a Double Paper Tape Sampler)."

(j) J. W. Chamblee, F. Arey, J. W. Powell, and E. Heckel. "Fluoride in the Ambient Air over the Pamlico Estuary in North Carolina." JAPCA, 21:484 (1980).

(k) D. F. S. Natusch, et al. "Sensitive Method for the Measurement of Atmospheric Hydrogen Sulfide." Anal. Chem., 44:2067 (1972).

(l) Intersociety Method No. 812. "Analytical Method for Hydrogen Sulfide in Air."

(m) R. S. Braman, J. M. Ammons, and J. L. Bricker. "Preconcentration and Determination of Hydrogen Sulfide in Air by Flame Photometric Detection." Anal. Chem., 50:992 (1978).

R. S. Braman. "Instrumentation Development for Ambient Reduced Forms of Sulfur in Air." EPA Report (Draft), EPA Grant No. R80-60-990-10, February 1980.

(n) T. L. C. de Souza, and S. P. Bhatia. "Development of Calibration System for Measuring Total Reduced Sulfur and Sulfur Dioxide in Ambient Concentrations in the Parts-per-Billion Range." Anal. Chem., 48:2234 (1976).

(o) R. K. Stevens, J. D. Mulik, A. E. O'Keeffe, and K. J. Krost. "Gas Chromatography of Reactive Sulfur Gases in Air at the Parts-per-Billion Level." Anal. Chem., 43:827 (1971).

R. E. Baumgardner, T. A. Clark, and R. K. Stevens. "Increased Specificity in the Measurement of Sulfur Compounds with the Flame Photometric Detector." Anal. Chem., 47:563 (1975).

RATIONALE FOR PSD MONITORING DE MINIMIS CONCENTRATIONS

The Monitoring De Minimis concentration for each regulated pollutant is based on 5 x LDC where LDC represents the lower detectable concentration of each pollutant in ambient air. For the gaseous criteria pollutants (CO, $NO_2$, $SO_2$, $O_3$), test data submitted in support of EPA designation of various automated methods (continuous analyzers) as reference or equivalent methods was reviewed to estimate the LDC for each pollutant and measurement principle. The estimated LDC values for these gaseous criteria pollutants are based on twice the standard deviation of repeated measurements at zero concentration. The LDC value for TSP is based on weighing unexposed and exposed filters to the nearest milligram and assumes a 1440 $m^3$ air sample. The LDC value for Pb is based on extrapolation of collaborative test data obtained with the EPA reference method. The LDC values for the non-criteria pollutants represent the lower limits of the measurement ranges reported for the various methodologies judged to be acceptable for PSD monitoring.

The use of 5 x LDC for the Monitoring De Minimis concentrations was chosen to realistically reflect pollutant levels at which low level concentrations or small incremental changes in pollutant concentrations can reasonably be determined. The factor 5 takes into account the measurement errors associated with the monitoring of these low pollutant levels or small incremental changes in pollutant concentration. These measurement errors arise from various sources such as sample collection (e.g., physical loss of pollutant during sampling, changes in collection efficiency at low levels); analytical measurement (e.g., zero and span drift of automated analyzer or analytical instrument, readability of recording device); calibration (e.g., inaccurate or nonreproducible low concentration pollutant standards); and interferences.

As an illustration of the estimated magnitude of these measurement errors, take the example of $SO_2$. The Monitoring De Minimis concentration for $SO_2$ is 0.0055 ppm. For the designated equivalent automated $SO_2$ methods, the error in an instantaneous measurement due to zero drift is typically $\pm$ 0.002 ppm. The effect of commonly occurring interferences such as $CO_2$ and $H_2O$ vapor can give rise to an additional measurement error of equal or sometimes greater magnitude depending on $SO_2$ and interferent concentrations and measurement principle. The combined error due to other measurement errors resulting from sampling, span drift, calibration error, and output recorder readability could reasonably be expected to be $\pm$ 0.002 ppm. Treating these as variances, the total uncertainty arising from these sources is estimated to be on the order of $\pm$ 0.0035 ppm ($\pm$ 0.002$\sqrt{3}$). On a relative basis this uncertainty can be rather significant when monitoring low levels of $SO_2$ or small incremental changes in $SO_2$ concentration. Similar examples could be given for the other gaseous criteria pollutants. Some of these measurement errors are random in nature (i.e., sometimes positive and sometimes negative) and would tend to be compensating to some extent, especially over long averaging times, resulting in measurements closer to the true ambient concentration. Instantaneous measurements or short-term averages would be subject to the higher uncertainty. Taking into account the above sources of error, operator induced error, and other unforeseen errors leads to the selection of 5 x LDC as a reasonable Monitoring De Minimis concentration. The selection of this value is somewhat judgmental in nature, but appears to be technically sound based on the assessment of measurement uncertainty as illustrated above.

The magnitude of measurement uncertainties for the particulate criteria pollutants and the non-criteria pollutants are expected to be correspondingly similar to that illustrated above given the LDC's of the specific methods in question. The monitoring methods judged to be acceptable for measurement of

ambient concentrations of the non-criteria pollutants have not always been subjected to the critical evaluation and performance and/or collaborative testing that has occurred for the criteria pollutants. Here, the selection of 5 x LDC is again judgmental but allows for a consistent approach to PSD monitoring of both criteria and non-criteria pollutants.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina 27711

DATE: May 27, 1980

SUBJECT: PSD Monitoring

FROM: Mr. Kenneth A. Rehme KAR
Methods Standardization Branch, QAD/EMSL (MD-77)

TO: Mr. Warren Peters
Control Programs Development Division, OAQPS (MD-15)

The initial list of acceptable measurement methods for the regulated non-criteria pollutants will consist of the methods marked by an asterisk (*) in the attached memorandum of May 20, 1980. The list, as well as individual method descriptions, will be available upon request by writing to the Quality Assurance Division (MD-77), Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

Attachment

cc: Mr. Thomas A. Clark
Dr. Thomas R. Hauser
Mr. Larry J. Purdue

EPA Form 1320-6 (Rev. 3-76)